

Properties of $Zn_xCd_{1-x}O$ films deposited by spray pyrolysis method

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Abstract

In this work, $Zn_xCd_{1-x}O$ films were prepared by ultrasonic spray pyrolysis (USP) technique onto glass substrates at a substrate temperature of 400 °C, using solution of cadmium acetate and zinc acetate salts. X-ray diffraction patterns of the films indicate that the $Zn_xCd_{1-x}O$ films have hexagonal and cubic structures for the constituent materials. A decrease in the average transmission with increasing quantity of the cadmium acetate dehydrate in the sprayed solution was observed. The photoconductivity transients were performed with the light of 360 nm. After light cut off, conductivity changed slowly, and the delay time was over thousands seconds. The films with $x=0.02$ and $x=0$ exhibited negative photoconductivity. Temperature dependent photoconductivity and dark conductivity measurements were performed and negative photoconductivity was also observed for the same films ($x=0.02$ and $x=0$). Photoluminescence measurements were performed and band to band excitations energies of $Zn_xCd_{1-x}O$ films were determined.

Introduction

ZnO and CdO, both are n-type semiconductor components [1]. In particular, zinc oxide is a promising material as gas sensor [2-4] varistors [5,6] and due to its large bandgap (of 3.3 eV), it is evidently used as an active window component of photovoltaic heterojunction thin film solar cells [7,8]. Its bandgap is wide enough to transmit most of the useful solar radiation in solar cells [9]. The cadmium oxide is used in the solar cell applications [10,11] because of its high electrical conductivity and optical transmittance in the visible region of the solar spectrum and is a candidate for a window layer on CdTe and CIS heterojunction also [12,13]. An important step to design ZnO based devices with high emitting efficiency is the band gap engineering in order for the fabrication of quantum wells that are necessary in devices such as light-emitting diode (LED) and laser diode (LD) [14-20]. The most commonly used approach to tune the band gap is to alloy CdO and ZnO to form a $Zn_{1-x}Cd_xO$ compound since CdO has a direct band gap [21], which shows a red shift of the luminescence peak with respect to that of ZnO [22]. The CdO thin films have a bandgap between 2.2 and 2.7 eV [23,24]. Bandgap values higher than 3 eV have been reported for CdO films deposited by CVD [25,26]. The ZnO thin films have stable electrical and optical properties; however, the CdO films have lower energy bandgap and a poor optical transmittance in the visible spectra region compared with those of ZnO films. The pure ZnO and CdO films have been studied by many research groups [27-33]. For the different applications mentioned before, it is especially important to study the alloy system of the two materials, as how the structure is affected when the composition changes since it is known that ZnO has a hexagonal wurtzite structure and the CdO a cubic one. In addition, it is interesting to determine how the bandgap varies with the concentration in the films between the one of ZnO equal to 3.3 eV [33] and that of CdO about 2.2 eV [23] with a low electrical resistivity.

Various growth techniques, including RF/DC magnetron sputtering, molecular beam epitaxy, pulsed laser deposition, thermal evaporation, sol-gel, chemical vapour deposition, and spray pyrolysis have been employed to obtain ZnO and CdO thin films on a different substrates. Among these, spray pyrolysis is a useful and alternative technique for obtaining thin films. It is of particular interest because of its simplicity, low cost and minimal waste production and it does not require a high vacuum apparatus. Spray pyrolysis involves spraying of a solution, containing soluble salts of the constituent atoms of the desired compounds onto heated substrates. For a sufficiently high temperature and a sufficiently volatile source compound, solvent evaporation and precipitate sublimation occur in succession. The vapors obtained diffuse towards the substrate where they react chemically in heterogeneous gas-solid phase to give final compound. The published works about the preparation and characterization of the transparent conducting $Zn_xCd_{1-x}O$ thin films are very limited, especially regarding the use of spray pyrolysis for its preparation [24,34-39]. So, our primarily aim in this work is to prepare $Zn_xCd_{1-x}O$ and investigate its properties.

Experimental

Our schematic diagram of USP setup is shown in Fig. 1. Microscope glass slides ($12.5 \times 12.5 \times 1$ mm³) were used as substrate. Before loading into the deposition system, the glass slides were soaked in acetone bath and washed in deionised water and dried. The spray solution was prepared by mixing appropriate volumes of zinc acetate dehydrate ($Zn(CH_3COO)_2 \cdot 2H_2O$) (0.1 M) and cadmium acetate dehydrate ($Cd(CH_3COO)_2 \cdot 2H_2O$) (0.1 M) dissolved in pure methanol. A small amount of acetic acid was added to solution to adjust the pH value to formation of hydroxides. The substrate temperature of 400 °C was controlled within ± 5 °C by using a Chrome-Nickel thermocouple kept on the metallic hot plate surface. The distance between the atomizer and the

substrate was kept fixed at 12 cm. The prepared solution was sprayed on the glass substrates using compressed purified air as a carrier gas with a flow rate of 5 ml/min. The gas evolving during the operation was removed using an evacuator.

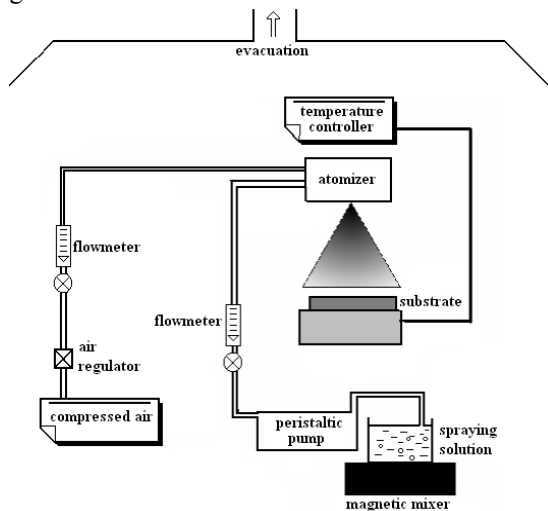


Figure 1. Schematic diagram of the ultrasonic spray pyrolysis system.

XRD spectra were obtained by a Rigaku Dmax-2200 model diffractometer at 40 keV and 36 mA. $\text{Cu K}\alpha$ (λ 1.5418 Å) radiation was used and the scanning angle 2θ was varied in the range between 30° and 90° . The optical transmission at normal incidence was obtained over the 350-1000 nm spectral range spectrophotometer by using UV enhanced Si photo diode. Quartz halogen lamp is used as a light source with suitable low-pass filters. A UV lamp is provided as the light source to perform photoresponse measurements. The magnitude of conductivity was deduced from current measurements at a bias of 50 mV. Photoluminescence measurements were performed at room temperature using a He-Cd laser as a light source at an excitation wavelength of 325 nm.

Results and Discussions

The sprayed thin films obtained have different colours, varying between colourless (white) for the ZnO to yellowish-caramel for the CdO films. They have strongly adherent to the substrates. The X-ray diffraction spectra of $\text{Zn}_x\text{Cd}_{1-x}\text{O}$ thin films for x from 0 to 0.1 have been realized in order to evaluate crystalline phase and crystallite orientation. The ZnO and CdO films are found to have different crystallographic structures. For the films with $x=0.1$ and $x=0$, the ZnO hexagonal and the CdO cubic structures were observed, respectively. The film with $x=0.08$ only the ZnO hexagonal phase and $x=0.02$ only the CdO cubic phase can be noticed, as seen in Fig. 2. In previous works, the clear presence of mixed crystallites of both ZnO and CdO compounds with hexagonal and cubic structures, respectively, was observed [37-39]. The films with $x=0.08$ and 0.02, the CdO and ZnO phases may exist in an amorphous state or in crystalline phase with very small crystallites as reported in reference [40], but this

phases were not observed clearly in the X-ray diffraction pattern.

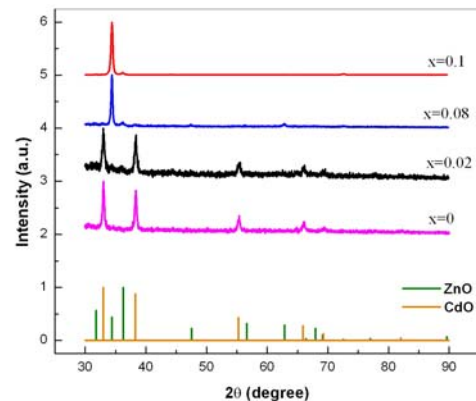


Figure 2. X-ray diffraction patterns for different compositions x of $\text{Zn}_x\text{Cd}_{1-x}\text{O}$ thin films.

Optical transmission spectra for the as deposited films are given in Fig. 3. Optical transmissions of the $\text{Zn}_x\text{Cd}_{1-x}\text{O}$ thin films have been taken at the ambient temperature, with consideration of a UV and visible energy range. The ZnO film is highly transparent and has an average transmission above 90% in the visible region and is characterized by a hard fall toward 3.27 eV. When the concentration of cadmium acetate dehydrate increases in the starting solution, one can observe in addition to the variation of the film colour (from transparent to yellowish-caramel color), a variation in the average transmission, which is about 50% for the pure CdO film. This behavior is expected because of the films become dull when x is decreased. For the films with $x=0$ and 0.02, clear absorption edges were not observed. Because of this, absorption edges of the films could not be analyzed.

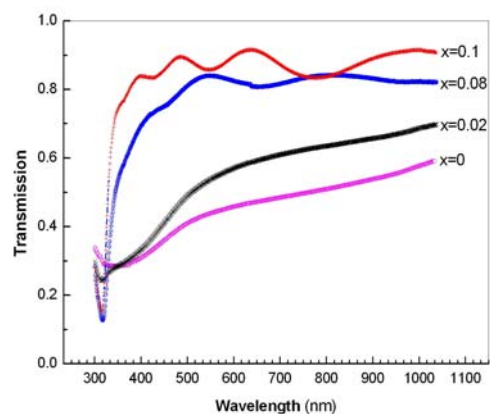
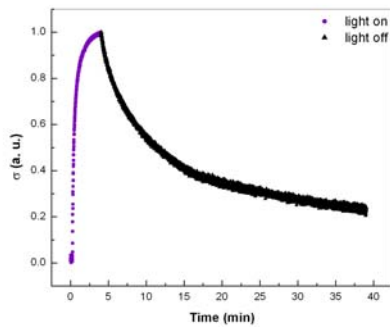


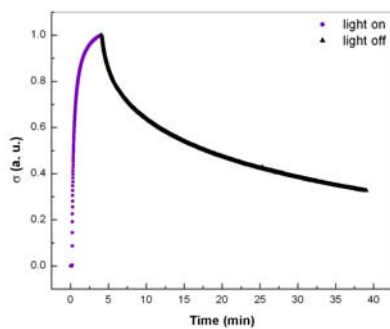
Figure 3. Transmissions of the $\text{Zn}_x\text{Cd}_{1-x}\text{O}$ thin films versus wavelength .

Shown in Fig. 3 are photoconductivity transients of the $\text{Zn}_x\text{Cd}_{1-x}\text{O}$ films. All measurements of the current were carried out under normal conditions at room temperature. An I-V curve was recorded before the

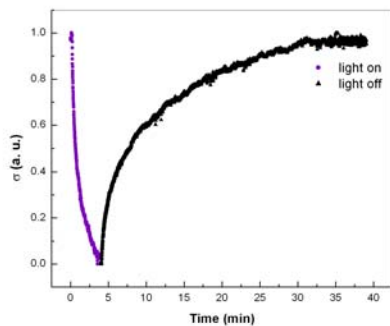
measurements started in order to ensure the Ohmic nature of the contacts.



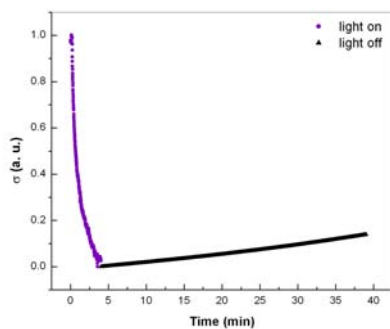
a)



b)



c)



d)

Figure 4. Photoconductivity transients of $Zn_xCd_{1-x}O$ films a) $x=0.1$ b) $x=0.08$ c) $x=0.02$ d) $x=0$.

Dc voltage was applied to the samples during the whole measurements and electrical current was measured with an electrometer. Generally, ZnO and CdO thin films show n-type conduction due to oxygen deficiencies and interstitial Zn and Cd ions which act as donors in the ZnO and CdO lattices. When oxygen is adsorbed by taking a free electron from the film in the dark and, then becomes negatively charged oxygen ions. Oxygen ions adhere to the surface and the crystalline interfaces of the film and form a chemically adsorbed surface state. Once the films conductivity have stabilized in the dark media, the photoconductivity can be recorded. All of the samples were directly irradiated by UV light for 4 min. The films with $x=0.1$ and $x=0.08$, were irradiated with uv light, electron-hole pair are produced. A large amount of photo generated electrons increase the carrier density, and the conductivity of the film increases quickly. On the other hand, photogenerated holes discharge negatively charged oxygen ions and oxygen is desorbed. As a result electrons are subsequently reintroduced into the conduction band, leading to an increase of conductivity. The oxygen photodesorption depletes most generated holes, and prohibits holes to recombine the conduction band electrons. However, electron hole generation rate is more rapid than oxygen photodesorption rate. Consequently, the conductivity increases (Fig. 4a and b). For $x=0.1$ and $x=0.08$ films, once irradiated with uv light, the photoconductivity rises more than 80% within 57 second and 59 second, respectively (Fig. 4a and b). When the uv light is off, electron hole recombination dominates and conductivity decrease quickly at first. Chemisorption of oxygen depletes free electron in the films, again. Typically oxygen chemisorption is slow compared to the oxygen photodesorption. It is obviously seen that relatively longer time is needed before conductivity comes to the initial value for the film with $x=0.08$.

It is determined that the current in the $Zn_xCd_{1-x}O$ films with $x=0.02$ and $x=0$ decreases when the films are illuminated, i.e., the effect of the negative photoconductivity is formed (Fig. 4c and d). When the light cut off in the dark, the kinetics of the current make up about 25 minutes and reaches initial value for the $x=0.02$ film. An analogous photo effect is also observed for pure CdO film but much more time requires for the film conductivity comes to initial value. In structures with n-type conductivity, this may lead to such a rare phenomenon as negative photoconductivity. In the majority of real cases, the conductivity increases upon illumination, because band-to-band illumination increases the concentration of free charge carriers. As one might expect, the conditions for occurrence of the negative photoconductivity are highly specialized. Observations were reported without explanations or else. Firstly, well defined observations on the negative photo effect in germanium have been reported by Stöckmann [41]. Negative photo effect was observed in modulation doped GaAs/AlGaAs heterojunctions,

unintentionally doped quantum wells of type InAs/AlSb, InAs/Al_{0.6}Ga_{0.4}Sb in which two dimensional electron gas appeared in the InAs well and α -Se layers [42-48]. Negative photoconductivity in Zn_xCd_{1-x}O and CdO films was not reported at other groups related to Zn_xCd_{1-x}O and CdO and also we don't attain article about negative photoconductivity of Zn_xCd_{1-x}O and CdO films. However, negative photoconductivity was clearly observed in our work as shown in Fig. 4c and d. Although, we didn't explain negative photoconductivity at the CdO and Zn_xCd_{1-x}O (x=0.02) films, we hope our results will provide valuable reference to the literature.

For investigation of heat or light is dominant on the conductivity properties, the heat and light are applied simultaneously.

Photosensitivity ($\Delta\sigma/\sigma_d = (\sigma_l - \sigma_d)/\sigma_d$) values of the films were calculated to access information about the sensitivity to the light at different temperatures. Photosensitivity values of the Zn_xCd_{1-x}O films depending on x values are given in Table 1. As seen in Table 1, $\Delta\sigma/\sigma_d > 0$ for the films with x=0.1 and x=0.08. In other words these films sensitive to the light ($\sigma_l > \sigma_d$). On the other hand, $\Delta\sigma/\sigma_d < 0$ for the films with x=0.02 and x=0. so, we can say that these films are negatively effected by light. As seen in Table 1, heat has not reversed sensitivity of the films to the light.

Table 1: Photosensitivity values of the Zn_xCd_{1-x}O films.

	x=0.1	x=0.08	x=0.02	x=0
300 K	0.154	2.163	-0.260	-0.441
320 K	0.127	1.962	-0.227	-0.459
350 K	0.084	1.758	-0.198	-0.416
375 K	0.061	1.651	-0.245	-0.416
400 K	0.042	1.542	-0.395	-0.457
420 K	0.032	1.406	-0.445	-0.469

Photoluminescence spectroscopy can be used to determine the fundamental bandgap of semiconductors since the most common radiative transition in semiconductor occur between states at the bottom of the conduction band and the top of the valance band. Fig. 5 shows the photoluminescence spectrum of Zn_xCd_{1-x}O (x= 0, 0.02, 0.08, 0.1) thin films deposited on glass substrate measured at room temperature. It can be noted that for x=0.1, the UV emission wavelength is located at 379 nm corresponding to the near band edge energy of 3.27 eV, which close to the reported optical band gap of ZnO [33]. UV emission of the film with x=0.08 has a red shift of 0.03 eV from that of pure ZnO film (3.27 eV).

Zn_xCd_{1-x}O is also regarded as an ideal material for ZnO-based devices. Fabrication and characterization of alloys such as Zn_xCd_{1-x}O are important from the viewpoint of band gap engineering as well as p-n junction. Being alloyed with CdO, which have narrower

band gap, the band gap of ZnO can be red shifted to the blue and even green-light spectral ranges.

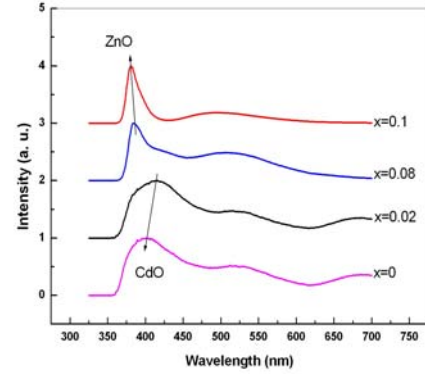


Figure 5. Photoluminescence spectra of the Zn_xCd_{1-x}O films.

Table 2 exhibits photoluminescence peak position energies of Zn_xCd_{1-x}O films depending on x. As seen in Table 2, photoluminescence peak position of pure CdO film (Zn_xCd_{1-x}O, x=0.1) is 3.11 eV. This forcefull peak is arises from radiative transition between states at the bottom of the conduction band and the top of the valance band of the CdO. Bandgap energies varying from 2.2 to 2.63 eV have been reported for CdO films deposited by various methods [49-51]. We have attained only two article which mentioned bandgap values higher than 3 eV have been reported for CdO films deposited by CVD [25, 26]. As seen in table 2, band gap emission energies of pure CdO and Zn_xCd_{1-x}O (x=0.02) are 3.11 eV and 3.03 eV, respectively.

Table 2: Photoluminescence peak position depending on x.

x	E _g (eV)
0.1	3.27
0.08	3.24
0.02	3.03
0	3.11

Conclusion

Zn_xCd_{1-x}O films were grown by USP technique and effect of concentration of the zinc acetate dihydrate and cadmium acetate dihydrate in the sprayed solution was investigated. Zn_xCd_{1-x}O films have hexagonal and cubic structures for the constituent materials. Optical transmissions of the films are found considerably dependent on the cadmium acetate dehydrate concentration of the spraying solution. The photoconductivity transients show that the films with x=0.1 and 0.08 are sensitive to the light. We reported negative photoconductivity was clearly observed in our work for the films with x= 0.02 and x=0. When heat and light are applied simultaneously, heat doesn't effect responsibility characteristics of the films. Band to band excitation energies was determined from the photoluminescence measurements and band gap of the pure CdO film is found 3.11 eV, interestingly. This

result agreement with the only two report in the literature.

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